Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
(Rev. 5-93)

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO **H 3609 PCT/US**

U S APPLICATION NO (if known sec 17 CFR 1 5)
10/088247

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/08923	**September 13, 2000**	**September 22, 1999**

TITLE OF INVENTION
METHOD FOR COLORING KERATIN FIBERS

APPLICANT(S) FOR DO/EO/US
Astrid Kleen, Andrea Saettler, Horst Hoeffkes, and Ralf Otto

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371

2. ☐ This a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. ☐ This express request to begin national examination procedures (35 U S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S.C. 371(b) and PCT Articles 22 and 39 (1).

4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ■ A copy of the International Application as filed (35 U.S C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau)
   b. ■ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. ■ A translation of the International Application into English (35 U S.C. 371(c)(2)).

7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made.

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S C. 371(c)(3)).

9. ■ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **UNEXECUTED**

10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ■ An Information Disclosure Statement under 37 CFR 1.97 and 1 98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3 28 and 3.31 is included

13. ■ A FIRST preliminary amendment
    ☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter

16. ☐ Other items or information..

Version with Markings to Show Changes Made;
Information Disclosure Citation (Form PTO-1449) and References; and
International Search Report

"Express Mail" mailing label number EL 615775295 US

U.S. Application No (If known see CFR1 30)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/088247	PCT/EP00/08923	H 3609 PCT/US

17. ■ The following fees are submitted:	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)). Search Report has been prepared by the EPO or JPO **$890.00**		
International preliminary examination fee paid to USPTO (37CFR 1.482) **$710.00**		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)) . . **$740.00**		
Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1 445(a)(2)) paid to USPTO. **$1,040.00**		
International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) . . . **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890 Order No. 02-0141	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).	$	

Claims	Number filed	Number Extra	Rate		
Total Claims	19- 20 =1	0	X 18.00	$	0
Independent Claims	5- 3 =1	2	X 84.00	$168 Order No 02-0141.01	00
Multiple dependent claims (s)(if applicable)		0	+ 280 00	$	00
TOTAL OF ABOVE CALCULATIONS ..... =				$ 1058	00
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1 27, 1 28)				$	
SUBTOTAL =				$	00
Processing fee of **$130.00** for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37CFR 1.492(f)). ..... +				$	
TOTAL NATIONAL FEE =				$	00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$ 1058	
				Amount to be: refunded	$----------
				charged	

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.
b. ■ Please charge my Deposit Account No **01-1250** in the amount of **$ 1058** to cover the above fees
A triplicate copy of this sheet is enclosed. Order No._____.
c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No **01-1250** A triplicate copy of this sheet is enclosed

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO. Henkel Corporation, Law Dept.
2500 Renaissance Blvd., Ste. 200
Gulph Mills, PA 19406.....

Kimberly R. Hild
SIGNATURE

Kimberly R. Hild
NAME ATTORNEY FOR APPLICANT

39,224
REGISTRATION NUMBER

Form PTO 1390 (REV 5-93)

PATENT
Docket No. H 3609 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Kleen, et al.

International Application No. PCT/EP00/08923
International Filing Date: September 13, 2000

Serial No. To be assigned **Examiner:** To be assigned

Filed: To be assigned **Art Unit:** To be assigned

Title: METHOD FOR COLORING KERATIN FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL 615775295 US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP00/08923 filed on September 13, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 45 486.8 filed on September 22, 1999.

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

-- BACKGROUND OF THE INVENTION -- .

On page 3, on a separate line between lines 14 and 15, please insert the following header:

--SUMMARY OF THE INVENTION--.

On page 3, on a separate line between lines 20 and 21, please insert the following header:

-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 38, line 1, please delete the heading “CLAIMS” and insert therefor:

-- What is claimed is: --

On a separate page, after page 39, please insert the enclosed Abstract of the Disclosure.

<u>In the Claims</u>

Please cancel Claims 1 to 17, without prejudice.

Please add the following new claims:

--18. (NEW) A process for coloring keratin fibers comprising applying to keratin fibers

(a) at least one colorant comprising at least one dye or dye precursor, or combinations thereof;

(b) at least one enzyme having transglutaminase activity; and

(c) at least one active substance having substrate activity for the enzyme having transglutaminase activity.

19. (NEW) The process of claim 18 wherein the enzyme having transglutaminase activity comprises a calcium-independent transglutaminase.

20. (NEW) The process of claim 18 wherein the active substance having substrate activity comprises at least one protein or protein hydrolyzate, or combinations thereof.

21. (NEW) The process of claim 20 wherein the active substance having substrate activity comprises casein, soya protein or wheat protein, or combinations thereof.

22. (NEW) The process of claim 18 wherein the active substance having substrate activity comprises a substance synthetically functionalized with an H_2N-R group or an H_2N-(CO)-R' group, wherein R and R' represent an unbranched C_{1-8} alkylene group.

23. (NEW) The process of claim 22 wherein the synthetically functionalized substance has at least one H_2N-$(CH_2)_4$ group.

24. (NEW) The process of claim 22 wherein the synthetically functionalized substance has at least one H_2N-(CO)-CH_2-CH_2 group.

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25. (NEW) The process of claim 18 wherein the colorant is applied to the keratin fibers, and then subsequently the enzyme having transglutaminase activity and the active substance having substrate activity are applied as a single composition to the keratin fibers.

26. (NEW) The process of claim 18 further comprising rinsing the enzyme having transglutaminase activity from the keratin fibers after a contact time of 3 minutes to 120 minutes.

27. (NEW) The process of claim 18 further comprising pretreating the keratin fibers with at least one pretreatment agent before applying the colorant, the enzyme having transglutaminase activity and the active substance having substrate activity.

28. (NEW) The process of claim 27 wherein the pretreatment agent comprises an oxidizing agent.

29. (NEW) The process of claim 27 wherein the pretreatment agent comprises a reducing agent.

30. (NEW) The process of claim 27 wherein the pretreatment agent comprises an enzyme different from the enzyme having transglutaminase activity.

31. (NEW) The process of claim 18 wherein the colorant, the enzyme having transglutaminase activity, and the active substance having substrate activity are applied simultaneously, or successively in any order.

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32. (NEW) The process of claim 18 wherein (i) the colorant and the enzyme having transglutaminase activity are applied to the keratin fibers in a single composition, (ii) the colorant and the active substance having substrate activity are applied to the keratin fibers in a single composition, or (iii) the active substance having substrate activity and the enzyme having transglutaminase activity are applied to the keratin fibers in a single composition.

33. (NEW) A method for improving washing fastness of colored keratin fibers comprising applying to keratin fibers that have been, are being, or will be colored:

(a) at least one enzyme having transglutaminase activity; and

(b) at least one active substance having substrate activity for the enzyme having transglutaminase activity.

34. (NEW) A multi-part kit for coloring keratin fibers comprising:

(a) a coloring composition comprising at least one colorant and at least one active substance having substrate activity to an enzyme having transglutaminase activity; and

(b) a second composition comprising at least one enzyme having transglutaminase activity.

35. (NEW) A multi-part kit for coloring keratin fibers comprising:

(a) a coloring composition comprising at least one colorant and at least one enzyme having transglutaminase activity; and

(b) a second composition comprising at least one active substance having substrate activity to the enzyme.

36. (NEW) A multi-part kit for coloring keratin fibers comprising:

(a) a coloring composition comprising at least one colorant;

(b) a second composition comprising at least one active substance having substrate activity to an enzyme having transglutaminase activity; and

(c) a third composition comprising at least one enzyme having transglutaminase activity.--

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REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 18 to 36 will be pending after entry of the present amendment. Claims 1 to 17 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein. Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made."

New Claims 18 to 36 replace original Claims 1 to 17, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
18	page 3, lines 15 to 30
19	page 4, lines 2 to 6
20, 21	page 4, line 22 to page 5, line 1
22, 23, 24	page 5, lines 10 to 15
25, 31, 32	page 6, lines 1 to 29
26	page 6, line 29 to page 7, line 2
27	page 21, lines 7 to 13
28	page 21, lines 14 to 16
29	page 22, lines 14 to 19
30	page 22, lines 23 to 29
33	page 31, line 29 to page 32, line 2
34, 35, 36	page 32, lines 3 to 14

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No new matter is added by the new claims or amendments to the specification.

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

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Abstract of the Disclosure

A method for coloring keratin fibers is provided. The method includes applying at least one colorant; at least one transglutaminase enzyme; and at least one active substance having substrate activity for the transglutaminase enzyme. The method improves the color fastness properties of colored keratin fibers. The present invention also provides multi-part kits containing the colorant, transglutaminase enzyme, and active substance.

Method for Coloring Keratin Fibers

The invention relates to a process for coloring keratin fibers.

Nowadays, human hair is treated in many different ways with hair-care preparations. Such treatments include, for example, the cleaning of hair with shampoos, the care and regeneration of hair with rinses and conditioners and the bleaching, coloring and shaping of hair with coloring and tinting formulations, wave formulations and styling preparations. Among these, formulations for modifying or shading the color of the hair occupy a prominent position. Disregarding blonding preparations which lighten the hair oxidatively by degrading the natural hair dyes, there are largely three types of preparations for changing the color of hair which are of importance in the coloring of hair:

So-called oxidation colorants are used for permanent, intensive colors with corresponding fastness properties. Oxidation colorants normally contain oxidation dye precursors, so-called primary intermediates and secondary intermediates. The primary intermediates form the actual dyes with one another or by coupling with one or more secondary intermediates under the influence of oxidizing agents or atmospheric oxygen. Although oxidation colorants are distinguished by excellent long-lasting coloring results, a mixture of a relatively large number of oxidation dye precursors normally has to be used for natural-looking colors. In many cases, substantive dyes are additionally used for shading. If the dyes formed during color development or directly used have clearly different fastness values (for example UV stability, fastness to perspiration, fastness to washing, etc.), a discernible and hence unwanted change of color can gradually occur. This phenomenon occurs to a greater extent if the hair style has hairs or hair zones damaged to different extents. One example of this are long hairs where the tips exposed for long periods to all kinds of

environmental influences are generally damaged to a greater extent than the relatively freshly regrown hair zones.

Colorants or tints containing substantive dyes as their coloring component are normally used for temporary colors. Substantive dyes are based on dye molecules which are directly absorbed onto the hair and do not require an oxidative process for developing the color. Dyes such as these include, for example, henna which has been used since ancient times for coloring the body and hair. Corresponding colors are generally far more sensitive to shampooing than the oxidative colors so that an often unwanted change of shade or even a visible "decoloration" then occurs very much more quickly.

Finally, a new coloring process has recently attracted considerable interest. In this process, precursors of the natural hair dye melanin are applied to the hair and then form "nature-like" dyes in the hair in the course of oxidative processes. One such process using 5,6-dihydroxyindoline as the dye precursor is described in **EP-B1 530 229**. If preparations containing 5,6-dihydroxyindoline are applied, in particular repeatedly, people with gray hair can be given back their natural hair color. Color development can be carried out with atmospheric oxygen as sole oxidizing agent so that no other oxidizing agent has to be used. In people with originally medium-blond to brown hair, the indoline may be used as sole dye precursor. By contrast, in people with originally red hair and, more particularly, dark to black hair, satisfactory results can often only be obtained by using other dye components as well, more particularly special oxidation dye precursors. In this case, too, the fastness of the colors can be problematical.

Accordingly, there has been no shortage of attempts to improve the fastness of colors on keratin fibers. One development direction is optimization of the dyes themselves or the synthesis of new modified dye molecules. Another development direction is the search for additives for

the colorants to increase the fastness of the colors. A known solution to the problem is to add UV filters to the colorant. These filters are applied to the hair together with the dye during the coloring process so that, in many cases, a distinct increase in the stability of the color to the effect of daylight or artificial light is obtained. In addition, the UV filters described in **DE-A1-198 53 11** also increase the fastness of the colors to washing.

It has now surprisingly been found that the fastness properties and particularly the fastness to washing of colors on keratin fibers can be significantly increased by a completely new enzymatic process.

Fastness to washing in the context of the present invention is understood to be the retention of the original color in regard to shade and/or intensity when the keratinic fiber is exposed to the repeated influence of water-based preparations, more particularly surfactant-containing preparations, such as shampoos.

In a first embodiment, therefore, the present invention relates to a process for coloring keratin fibers with dyes and/or dye precursors in which (A) at least one enzyme of the transglutaminase type and (B) at least one active substance with substrate activity for the enzyme are applied to the fibers.

Keratin fibers in the context of the invention are understood to include pelts, wool, feathers and in particular human hair.

An enzyme which is preferably used in the process according to the invention is transglutaminase (official name: protein glutamine gamma-glutamyltransferase; EC 2.3.2.13). This enzyme preferentially catalyzes the reaction of the amino acid moiety glutamine in a protein with an alkylamine to form an N5-alkylglutamine protein with release of ammonia. A preferred natural alkylamine which plays a role in this reaction is the amino acid lysine or the amino acid moiety lysine in a protein.

In principle, any enzymes with transglutaminase activity are suitable for carrying out the present invention. Suitable enzymes of this type are,

for example, transglutaminases obtained from guinea pig liver, *Physarum polycephalum*, *Medicago savica* or *Bacillus subtilus*. The calcium-independent transglutaminases described, for example, in **EP 726 317 A2** and in **EP 397 606 A1** which are marketed by Ajinomoto are particularly preferred. The Ajinomoto products Activa® WM and EB are preferred, Activa® WM being particularly preferred.

The use of transglutaminases in cosmetic formulations is already known from the literature. For example, **US 5,490,980** describes a composition for treating human skin, hair or nails with which active substances containing a primary amino group are added onto the glutamine components of the skin, hair or nails by transglutaminase. However, there is nothing in this document which points to the subject of the present invention or to the increase in the fastness of hair colors to washing.

In the context of the invention, an active substance with substrate activity is any substance which can be added onto the hair by the transglutaminase. This can be done, for example, by crosslinking the active substances with substrate activity with one another, i.e. by forming a kind of membrane around the hair. However, this can also be done with advantage by covalent bonding of the active substances with substrate activity to the lysine and/or glutamine components of the hair.

In a first preferred embodiment of the present invention, naturally occurring substances are used as active substances with substrate activity. Proteins, protein hydrolyzates and derivatives thereof are particularly suitable for this purpose. Protein hydrolyzates are product mixtures obtained by acid-, base- or enzyme-catalyzed degradation of proteins.

According to the invention, proteins and protein hydrolyzates of both vegetable and animal origin may be used.

Animal proteins are, for example, elastin, collagen, keratin, silk and milk protein. Examples of proteins of vegetable origin are soya, almond,

pea, alga, potato and wheat protein.

Although proteins as such are preferably used, other natural active substances with substrate activity, such as for example peptides, amino acids and corresponding derivatives, may also be used instead. Derivatives of the protein hydrolyzates, for example in the form of their fatty acid condensation products or cationic derivatives, may also be used but are less preferred.

Casein, soya protein and wheat protein are particularly preferred, casein being most particularly preferred.

In a second preferred embodiment of the invention, substances synthetically functionalized with an H_2N-R group or an H_2N-(CO)-R' group, where R and R' stand for an unbranched C_{1-8} alkylene group, are used as active substances with substrate activity. Particularly preferred functional groups are the groups H_2N-$(CH_2)_4$ and H_2N-(CO)-CH_2-CH_2- derived from lysine or glutamine.

In addition, monomers such as, for example, lysine and glutamine may be used in accordance with the invention as active substances with substrate activity. They may be used both as an additional active substance with substrate activity and as sole component. In a preferred embodiment of the invention, both proteins and corresponding monomers may be used during the process to improve fastness to washing by fairly rapidly building up a dense network of the active substances with substrate activity.

The active substances with substrate activity are present in the compositions used in accordance with the invention in quantities of preferably 0.005 to 10% by weight, based on the composition as a whole. Quantities of 0.01 to 2% by weight are particularly preferred. The ratio by weight of the transglutaminase type enzyme to the active substance with substrate activity is preferably 1:4000 to 1:1 and more preferably 1:2000 to 1:50.

So far as the time sequence of the coloring process is concerned, the invention is not subject to any limitations. Besides the possibility of simultaneously applying all three components (coloring preparation, transglutaminase type enzyme and active substance with substrate activity) to the hair, it is possible in principle to apply three separate preparations containing (a) the coloring preparation, (b) the active substance with substrate activity and (c) the transglutaminase type enzyme successively in any order to the fibers. In a preferred embodiment, the three components (a), (b) and (c) are applied to the fibers in that order. The fibers may be rinsed after the application of component (a). According to the invention, the components may also be separately applied in the order (a) → (c) → (b). In this case, however, the time interval between the individual steps and particularly between the steps (b) and (c) should not be too long to ensure that the fibers do not dry between the steps.

Although this three-stage process does produce the desired effects, it may be preferred to carry out the process according to the invention in two stages because two-stage processes are easier to carry out. In the two-stage processes, it has proved to be of advantage separately to apply the coloring preparation and the preparation containing the transglutaminase type enzyme. The active substance with substrate activity may be applied both together with the coloring preparation and together with the enzyme preparation. In a particularly preferred embodiment, the active substance with substrate activity is applied together with the enzyme preparation.

The enzyme preparation is normally applied to the hair while it is still wet after the actual hair coloring process, i.e. after the oxidation colorant has been rinsed out, after the colorant containing "nature-like" dye precursors has been rinsed out or after application of the tinting preparation containing only substantive dyes. Although in principle the preparation can remain on the hair, a preferred embodiment of the process according to the

invention is characterized in that the preparation containing the enzyme is rinsed out after a contact time of 3 to 120 minutes. The preparation may be rinsed out with clean water. Contact times of 15 to 30 minutes have proved to be sufficient in most cases.

Irrespective of the nature of the coloring process, it has proved to be of advantage to apply the enzyme preparation at a temperature of 20 to 55°C and more particularly at a temperature of 35 to 50°C.

In principle, there are no limits to the nature of the enzyme preparation. According to the invention, aqueous, alcoholic and oily preparations and mixtures thereof are particularly suitable. Aqueous preparations are particularly preferred. These may be, for example, solutions, dispersions, emulsions (water-in-oil emulsions, oil-in-water emulsions and multiple emulsions and PIT emulsions). The pH value of these preparations is generally in the range from 2 to 10, preferably in the range from 4 to 9 and more preferably in the range from 6 to 8.

In a preferred embodiment of the present invention, the enzyme preparations are formulated as a thickened solution. To this end, the preparations are thickened with thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrins, clays, for example bentonite, or fully synthetic hydrocolloids, for example polyvinyl alcohol or even polyacrylic acid polymers. In a particularly preferred embodiment, the enzyme preparations are formulated with low viscosities.

Besides the enzyme and optionally the active substance with substrate activity, the enzyme preparations may contain all the usual constituents suitable for the treatment of keratin fibers, particularly human hair. Aqueous preparations are preferred. Aqueous preparations in the context of the invention are preparations which contain at least 50% by

weight water, based on the preparation as a whole.

It has proved to be of advantage for the enzyme preparation to contain at least one surfactant. Suitable surfactants are both anionic, ampholytic, zwitterionic or nonionic surfactants and cationic surfactants. If necessary, the expert may carry out simple preliminary tests to determine whether the various surfactants have any effect on the activity of the transglutaminase type enzyme.

A preferred embodiment of the invention is characterized by the use of a combination of anionic and nonionic surfactants or a combination of anionic and amphoteric surfactants.

However, it has proved to be of advantage in individual cases to select the surfactants from amphoteric or nonionic surfactants because they generally have less influence on the coloring process according to the invention.

Suitable anionic surfactants in the compositions according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide and hydroxyl groups may also be present in the molecule.

Nonionic surfactants contain, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide to linear fatty alcohols containing 8 to 22 carbon atoms, to fatty acids containing 12 to 22 carbon atoms and to alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C_{12-22} fatty acid monoesters and diesters of products of the addition

of 1 to 30 moles of ethylene oxide to glycerol,

- C_{8-22} alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- products of the addition of 5 to 60 moles of ethylene oxide to castor oil and hydrogenated castor oil.

Preferred nonionic surfactants are alkyl polyglycosides corresponding to the general formula $R^1O-(Z)_x$. These compounds are characterized by the following parameters.

The alkyl group R^1 contains 6 to 22 carbon atoms and may be both linear and branched. Primary linear and 2-methyl-branched aliphatic groups are preferred. Such alkyl groups are, for example, 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl. 1-Octyl, 1-decyl, 1-lauryl and 1-myristyl are particularly preferred. Where so-called "oxo alcohols" are used as starting materials, compounds with an odd number of carbon atoms in the alkyl chain predominate.

The alkyl polyglyosides suitable for use in accordance with the invention may, for example, contain only one particular alkyl group R^1. However, such compounds are normally prepared from natural fats and oils or mineral oils. In this case, mixtures corresponding to the starting compounds or corresponding to the particular working up of these compounds are present as the alkyl groups R.

Particularly preferred alkyl polyglycosides are those in which R^1 consists

- essentially of C_8 and C_{10} alkyl groups,
- essentially of C_{12} and C_{14} alkyl groups,
- essentially of C_8 to C_{16} alkyl groups or
- essentially of C_{12} to C_{16} alkyl groups.

Any mono- or oligosaccharides may be used as the sugar unit Z. Sugars containing 5 or 6 carbon atoms and the corresponding oligosaccharides are normally used. Examples of such sugars are glucose,

fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. Preferred sugar units are glucose, fructose, galactose, arabinose and sucrose; glucose is particularly preferred.

The alkyl polyglycosides suitable for use in accordance with the invention contain on average 1.1 to 5 sugar units. Alkyl polyglycoside with x values of 1.1 to 1.6 are preferred. Alkyl glycosides where x is 1.1 to 1.4 are most particularly preferred.

Besides acting as surfactants, the alkyl glycosides may also be used to improve the fixing of perfume components to the hair. Accordingly, in cases where the effect of the perfume oil on the hair is intended to last longer than the duration of the hair treatment, alkyl glycosides will preferably be used as another ingredient of the preparations according to the invention.

Alkoxylated homologs of the alkyl polyglycosides mentioned may also be used in accordance with the invention. These homologs may contain on average up to 10 ethylene oxide and/or propylene oxide units per alkyl glycoside unit.

Zwitterionic surfactants may also be used, particularly as co-surfactants. In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one $-COO^{(-)}$ or $-SO_3^{(-)}$ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinates, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinates, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is

the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Also suitable, particularly as co-surfactants. are ampholytic surfactants. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8-18} alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO_3H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl aminopropionate, cocoacyl aminoethyl aminopropionate and C_{12-18} acyl sarcosine.

According to the invention, the cationic surfactants used are particularly those of the quaternary ammonium compound, esterquat and amidoamine type.

Preferred quaternary ammonium compounds are ammonium halides, more particularly chlorides and bromides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride and the imidazolium compounds known under the INCI names of Quaternium-27 and Quaternium-83. The long alkyl chains of the above-mentioned surfactants preferably contain 10 to 18 carbon atoms.

Esterquats are known substances which contain both at least one ester function and at least one quaternary ammonium group as structural element. Preferred esterquats are quaternized ester salts of fatty acids

with triethanolamine, quaternized ester salts of fatty acids with diethanol alkylamines and quaternized ester salts of fatty acids with 1,2-dihydroxypropyl dialkylamines. Such products are marketed, for example, under the names of Stepantex®, Dehyquart® and Armocare®. The products Armocare® VGH-70, an N,N-bis-(2-palmitoyloxyethyl)-dimethyl ammonium chloride, and Dehyquart® F-75 and Dehyquart® AU-35 are examples of such esterquats.

The alkyl amidoamines are normally prepared by amidation of natural or synthetic fatty acids and fatty acid cuts with dialkyl aminoamines. A compound from this group particularly suitable for the purposes of the invention is the stearamidopropyl dimethylamine obtainable under the name of Tegoamid® S 18.

The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with different alkyl chain lengths dependent upon the particular raw material are obtained.

The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products with a narrow homolog distribution. Products with a "normal" homolog distribution are mixtures of homologs which are obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

In addition, the enzyme preparations used in accordance with the invention preferably contain at least one oil component.

Oil components suitable for the purposes of the invention are, in principle, any water-insoluble oils and fatty compounds and mixtures thereof with solid paraffins and waxes. According to the invention, water-insoluble substances are defined as substances of which less than 0.1% by weight dissolves in water at 20°C. The melting point of the individual oil or fatty components is preferably below about 40°C. Oil and fatty components which are liquid at room temperature, i.e. below 25°C, can be particularly preferred for the purposes of the invention. However, where several oil and fatty components and optionally solid paraffins and waxes are used, it is generally sufficient if the mixture of the oil and fatty components and optionally paraffins and waxes satisfies these requirements.

A preferred group of oil components are vegetable oils. Examples of such oils are sunflower oil, olive oil, soya oil, rapeseed oil, almond oil, jojoba oil, orange oil, wheatgerm oil, peach kernel oil and the liquid fractions of coconut oil.

However, other triglyceride oils, such as the liquid fractions of bovine tallow, and synthetic triglyceride oils are also suitable.

Another group of compounds particularly preferred for use as oil components in accordance with the invention are liquid paraffin oils and synthetic hydrocarbons and di-n-alkyl ethers containing a total of 12 to 36 carbon atoms and, more particularly, 12 to 24 carbon atoms, such as for example di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether, di-n-dodecyl ether, n-hexyl-n-octyl ether, n-octyl-n-decyl ether, n-decyl-n-undecyl ether, n-undecyl-n-dodecyl ether and n-hexyl-n-undecyl ether and ditert.butyl ether, diisopentyl ether, di-3-ethyldecyl ether, tert.butyl-n-octyl ether, isopentyl-n-octyl ether and 2-methylpentyl-n-octyl ether. The compounds 1,3-di-(2-ethylhexyl)-cyclohexane and di-n-octyl ether obtainable as commercial products (Cetiol® S and Cetiol® OE, respectively) can be preferred.

Other oil components suitable for use in accordance with the invention are fatty acid and fatty alcohol esters. The monoesters of fatty acids with alcohols containing 3 to 24 carbon atoms are preferred. This group of substances are products of the esterification of fatty acids containing 8 to 24 carbon atoms such as, for example, caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof obtained, for example, in the pressure hydrolysis of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerization of unsaturated fatty acids with alcohols such as, for example, isopropyl alcohol, caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and the technical mixtures thereof obtained, for example, in the high-pressure hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fraction in the dimerization of unsaturated fatty alcohols. According to the invention, isopropyl myristate, isononanoic acid C_{16-18} alkyl ester (Cetiol® SN), stearic acid-2-ethylhexyl ester (Cetiol® 868), cetyl oleate, glycerol tricaprylate, cocofatty alcohol caprate/caprylate and n-butyl stearate are particularly preferred.

Other oil components suitable for use in accordance with the invention are dicarboxylic acid esters, such as di-n-butyl adipate, di-(2-ethylhexyl)-adipate, di-(2-ethylhexyl)-succinate and diisotridecyl acelate, and diol esters, such as ethylene glycol dioleate, ethylene glycol diisotri-

decanoate, propylene glycol di-(2-ethylhexanoate), propylene diisostearate, propylene glycol dipelargonate, butanediol diisostearate and neopentyl glycol dicaprylate, and also complex esters, for example diacetyl glycerol monostearate.

Finally, fatty alcohols containing 8 to 22 carbon atoms may also be used as oil components in accordance with the invention. The fatty alcohols may be saturated or unsaturated and linear or branched. Examples of fatty alcohols suitable for use in accordance with the invention are decanol, octanol, octenol, dodecenol, decenol, octadienol, dodecadienol, decadienol, oleyl alcohol, erucyl alcohol, ricinolyl alcohol, stearyl alcohol, isostearyl alcohol, cetyl alcohol, lauryl alcohol, myristyl alcohol, arachidyl alcohol, capryl alcohol, capric alcohol, linoleyl alcohol, linolenyl alcohol and behenyl alcohol and Guerbet alcohols thereof (this list is purely exemplary and is not intended to limit the invention in any way). However, the fatty alcohols emanate from preferably natural fatty acids, normally being obtained from the esters of the fatty acids by reduction. According to the invention, it is also possible to use the fatty alcohol cuts which are produced by reduction of naturally occurring triglycerides, such as bovine tallow, palm oil, peanut oil, rapeseed oil, cottonseed oil, soybean oil, sunflower oil and linseed oil, or fatty acid esters formed from the transesterification products thereof with corresponding alcohols and which therefore represent a mixture of different fatty alcohols.

In a preferred embodiment, the enzyme preparations used in accordance with the invention contain a care component. This care component is preferably selected from cationic polymers and silicones.

A first group of cationic polymers are the so-called "temporarily cationic" polymers. These polymers normally contain an amino group which is present as a quaternary ammonium group and hence cationically at certain pH values.

Among the cationic polymers, the permanently cationic polymers are

preferred. According to the invention, "permanently cationic polymers" are polymers which contain a cationic group irrespective of the pH of the composition. These are generally polymers which contain a quaternary nitrogen atom, for example in the form of an ammonium group. Preferred cationic polymers are, for example,

- the quaternized cellulose derivatives commercially available under the names of Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and Polymer JR® 400 are preferred quaternized cellulose derivatives,
- polysiloxanes containing quaternary groups such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning® 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, Quaternium-80),

  cationic guar derivatives such as, in particular, the products marketed under the names of Cosmedia® Guar and Jaguar®,
- polymeric dimethyl diallyl ammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid. The products commercially available under the names of Merquat® 100 (poly(dimethyl diallylammonium chloride)) and Merquat® 550 (dimethyl diallylammonium chloride/acrylamide copolymer) are examples of such cationic polymers,
- copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate such as, for example, vinyl pyrrolidone/dimethylamino methacrylate copolymers quaternized with diethyl sulfate. Such compounds are commercially available under the name of Gafquat® 734 and Gafquat® 755,

- The vinyl pyrrolidone/vinyl imidazolinium methochloride copolymers commercially available under the name of Luviquat® FC 370, FC 550, FC 905 and HM 552,
- quaternized polyvinyl alcohol;

and the polymers containing quaternary nitrogen atoms in the main polymer chain known under the names of

- Polyquaternium 2,
- Polyquaternium 17,
- Polyquaternium 18 and
- Polyquaternium 27.

Other suitable cationic polymers are the polymers known by the names of Polyquaternium-24 (commercial product: Quatrisoft® LM 200 for example), Polyquaternium-32, Polyquaternium-35 and Polyquaternium-37 (commercial products: Salcare® SC 92 and Salcare® SC 95). Also suitable for use in accordance with the invention are the vinyl pyrrolidone copolymers known by the commercial names of Copolymer 845 (manufacturer: ISP), Gaffix® VC 713 (manufacturer: ISP), Gafquat® ASCP 1011, Gafquat® HS 110, Luviquat® 8155 and Luviquat® MS 370.

According to the invention preferred cationic polymers are quaternized cellulose derivatives, polymeric dimethyl diallyl ammonium salts, Polyquaternium-27 and copolymers thereof and polymers of the Polyquaternium-2 type. Cationic cellulose derivatives, more particularly the commercial product Polymer® JR 400, and polymers of the Polyquaternium-2 type, more particularly the commercial product Mirapol® A-15, are most particularly preferred cationic polymers.

The cationic polymers are present in the compositions used in accordance with the invention in quantities of preferably 0.05 to 5% by weight, based on the composition as a whole. Quantities of 0.1 to 5% by weight are particularly preferred.

Amphopolymers may also be used as a care component in

combination with or alternatively to the cationic polymers. Amphopolymers are amphoteric polymers, i.e. polymers which contain both free amino groups and free -COOH or -SO_3H groups in the molecule and which are capable of forming inner salts, zwitterionic polymers which contain quaternary ammonium groups and $-COO^-$ or -SO_3^- groups in the molecule and polymers which contain –COOH- or SO_3H groups and quaternary ammonium groups. One example of an amphopolymer suitable for use in accordance with the invention is the acrylate resin commercially available as Amphomer® which is a copolymer of tert.butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)-acrylamide and two or more monomers from the group consisting of acrylic acid, methacrylic acid and simple esters thereof. Other preferred amphopolymers consist of unsaturated carboxylic acids (for example acrylic and methacrylic acid), cationically derivatized unsaturated carboxylic acids (for example acrylamidopropyl trimethyl ammonium chloride) and optionally other ionic or nonionic monomers of the type disclosed, for example, in **DE-OS 39 29 973** and the prior art literature cited therein. According to the invention, terpolymers of acrylic acid, methyl acrylate and methacrylamidopropyl trimonium chloride, which are commercially available under the name of Merquat® 2001 N, and the commercial product Merquat® 280 are particularly preferred ampho-polymers.

Other care substances suitable for used in accordance with the invention are silicone oils and silicone gums, more particularly dialkyl and alkylaryl siloxanes such as, for example, dimethyl polysiloxane and methylphenyl polysiloxane and alkoxylated and quaternized analogs thereof. Examples of such silicones are the products marketed by Dow Corning under the names of DC 190, DC 200 and DC 1401 and the commercial products DC 344 and DC 345 of Dow Corning, Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning® 929 emulsion (containing a hydroxylamino-modified silicone

which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil® Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80) and the commercial product Fancorsil® LIM-1. A suitable anionic silicone oil is the product Dow Corning® 1784.

Besides the transglutaminase type enzyme and the other preferred components mentioned above, the enzyme preparations may basically contain any other components known to the expert for such cosmetic preparations.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- structurants, such as maleic acid and lactic acid,
- hair-conditioning compounds, such as phospholipids, for example soybean lecithin, egg lecithin and kephalins,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- fiber structure improvers, more particularly mono-, di- and oligosaccharides such as, for example, glucose, galactose, fructose and lactose,
- quaternized amines, such as methyl-1-alkylamidoethyl-2-alkylimidazolinium methosulfate,
- defoamers, such as silicones,
- dyes for coloring the composition,
- antidandruff agents, such as Piroctone Olamine, Zinc Omadine and Climbazol,
- light filters, more particularly derivatized benzophenones, cinnamic acid derivatives and triazines,

- substances for adjusting the pH value, such as for example the usual acids, more particularly edible acids and bases,
- active principles, such as allantoin, pyrrolidone carboxylic acids and salts thereof and bisabolol,
- vitamins, provitamins and vitamin precursors, more particularly those of groups A, B_3, B_5, B_6, C, E, F and H,
- plant extracts, such as the extracts of green tea, oak bark, stinging nettle, hamamelis, hops, camomile, burdock root, horse willow, hawthorn, lime blossom, almond, aloe vera, pine needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, creeping thyme, yarrow, thyme, balm, restharrow, coltsfoot, hibiscus, meristem, ginseng and ginger root ,
- cholesterol,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax and paraffins,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA, β-alanine diacetic acid and phosphonic acids,
- swelling and penetration agents, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates,
- opacifiers, such as latex, styrene/PVP and styrene/acrylamide copolymers,
- pearlizers, such as ethylene glycol mono- and distearate and PEG-3-distearate,
- pigments,
- stabilizers for hydrogen peroxide and other oxidizing agents,

- propellents, such as propane/butane mixtures, N_2O, dimethyl ether, CO_2 and air.

Information on other optional components and the quantities in which they are used can be found in the reference books known to the expert, for example Kh. Schrader, **Grundlagen und Rezepturen der Kosmetika, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989**.

Although, in principle, the effect according to the invention can be observed in hair of any kind, it has been found that the process according to the invention can be applied with particular advantage to pretreated hair. In a model which is not intended to limit the invention in any way, it is assumed that the addition of the active substances with substrate activity can be improved if the surface of the hair has more functional groups exposed by the pretreatment.

In a first embodiment of the present invention, this pretreatment may be an oxidative process. Both inorganic and organic compounds may be used as oxidizing agents.

Preferred inorganic compounds are hydrogen peroxide, bromates, chlorates, iodates, perchlorates, peroxodisulfates, chlorites, bromites, perborates, peroxocarbonates, peroxodiphosphates and iron(III), cerium(IV) and ruthenium(III) salts. If the oxidizing agent is a salt, the counterion is selected from the physiologically compatible ions. In the case of the cations, these ions are preferably alkali metal ions, more particularly potassium and sodium ions, alkaline earth metal ions, more particularly magnesium ions, aluminium ions and ammonium and mono-, di- and triethanolammonium ions. In the case of the anions, they are preferably sulfate, halide (more particularly chloride), phosphate, acetate, tartrate and citrate ions.

Particularly preferred inorganic oxidizing agents are hydrogen peroxide, sodium bromate, sodium perborate, sodium percarbonate and ammonium, sodium and potassium peroxodisulsulfate. Hydrogen peroxide

is most particularly preferred.

Preferred organic compounds are

- benzoquinones such as, for example, 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone, 2-chloro-1,4-benzoquinone, 2-dimethylamino-1,4-benzoquinone, 2,3-dimethyl-1,4-benzoquinone, 1,4-naphtoquinone and 1,2-naphthoquinone,
- percarbamide,
- products of the addition of hydrogen peroxide onto melamine, polyvinyl pyrrolidone and urea,
- flavine derivatives and
- azodicarbonamide.

Particularly preferred organic compounds are benzoquinones, percarbamide and melamine perhydrate.

In a second embodiment of the present invention, however, the pretreatment may also be a reductive process. Examples of suitable reducing agents are thioglycolic acid, thiolactic acid, thioglycerol, mercaptopropionic acid, sodium hydrogen sulfite, ammonium hydrogen sulfite, cysteamine, dithiothreitol, thiomalic acid and α-mercaptoethyl-sulfonic acid.

Particularly preferred reducing agents are thioglycolic acid and esters thereof, sodium hydrogen sulfite, ammonium hydrogen sulfite and cysteamine.

In a third embodiment of the present invention, the pretreatment may even be carried out by enzymes. According to the invention, protein disulfite isomerase, amylase, protease, esterase, pronase and lipase have proved to be particularly suitable. Preferred proteases are the serine proteases such as, for example, trypsin, chymotrypsin or subtilisin (for example Alcalase®, a product of Novo Nordisk; Blap®, a product of Henkel KGaA) and the cystein proteases.

The pretreatment may be carried out in a separate step immediately

before the coloring process or even some time beforehand. For example, a permanent wave treatment or a previous oxidative coloring or lightening of the hair may provide the effect required by the pretreatment. This effect can also be observed on hair that has been damaged by environmental influences, for example UV light.

Since fibers thus pretreated are more porous, known coloring processes are often attended by the problem that the color uptake and the fastness properties of the colors obtainable on such fibers are clearly impaired. Accordingly, an advantage of the hair coloring process according to the invention is that it enables colors with distinctly improved fastness to washing to be obtained on hair thus pretreated.

According to the invention, the coloring process may be any of the processes known to the expert where a colorant is applied to the optionally moistened hair and is either left on the hair for a few minutes to ca. 45 minutes and then rinsed out with water or a surfactant-containing preparation or is left entirely on the hair. In this connection, reference is specifically made to the known works, for example the above-cited book by Kh. Schrader, which reproduce the corresponding knowledge of the expert.

The composition of the coloring or tinting preparation is not subject to any basic limitations. Suitable dye (precursor)s are

- oxidation dye precursors of the primary and secondary intermediate types,
- natural and synthetic substantive dyes and
- precursors of nature-like dyes, such as indole and indoline derivatives

and mixtures of representatives of one or more of these groups.

Oxidation dye precursors of the primary intermediate type are normally primary aromatic amines with another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-

tetraaminopyrimidine and derivatives thereof. Suitable primary intermediates are, for example, p-phenylenediamine, p-toluylenediamine, p-aminophenol, o-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2-hydroxymethylaminomethyl-4-aminophenol, bis-(4-aminophenyl)-amine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxy-methyl-4-aminophenol, 4-amino-2-(diethylamino)-methyl)-phenol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4-aminophenyl)-diazacycloheptane, 1,3-bis-(N-(2-hydroxyethyl)-N-(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)-phenol, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane and 4,5-diaminopyrazole derivatives according to **EP 0 740 931** or **WO 94/08970**, for example 4,5-diamino-1-(2'-hydroxyethyl)-pyrazole. Particularly advantageous primary intermediates are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine and 4-hydroxy-2,5,6-triaminopyrimidine.

m-Phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives are generally used as oxidation dye precursors of the secondary intermediate type. Examples of such secondary intermediates are

- m-aminophenol and derivatives thereof such as, for example, 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetylamino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-

cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,

- o-aminophenol and derivatives thereof,
- m-diaminobenzene and derivatives thereof such as, for example, 2,4-diaminophenoxyethanol, 1,3-bis-(2,4-diaminophenoxy)-propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2,4-diaminophenyl)-propane, 2,6-bis-(2-hydroxyethylamino)-1-methyl-benzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,
- o-diaminobenzene and derivatives thereof such as, for example, 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,
- di- and trihydroxybenzene derivatives such as, for example, resorcinol, resorcinol monomethyl ether, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,
- pyridine derivatives such as, for example, 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diamino-pyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
- naphthalene derivatives such as, for example, 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihdroxynaphthalene, 1,7-dihdroxy-naphthalene, 1,8-dihdroxynaphthalene, 2,7-dihdroxynaphthalene and 2,3-dihdroxynaphthalene,
- morpholine derivatives such as, for example, 6-hydroxybenzomorpholine and 6-aminobenzomorpholine,
- quinoxaline derivatives such as, for example, 6-methyl-1,2,3,4-tetrahydroquinoxaline,

- pyrazole derivatives such as, for example, 1-phenyl-3-methylpyrazol-5-one,
- indole derivatives such as, for example, 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole,
- methylenedioxybenzene derivatives such as, for example, 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene.

Particularly suitable secondary intermediates are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol and 2,6-dihydroxy-3,4-dimethylpyridine.

Substantive dyes are normally nitrophenylenediamines, nitroaminophenols, azo dyes, anthraquinones and indophenols. Particularly suitable substantive dyes are the compounds known under the International names or commercial names of HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17 and also 1,4-bis-(β-hydroxyethyl)-amino-2-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, hydroxyethyl-2-nitrotoluidine, picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

Naturally occurring substantive dyes are, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet, may also be used to obtain further shades.

Neither the oxidation dye precursors nor the substantive dyes have

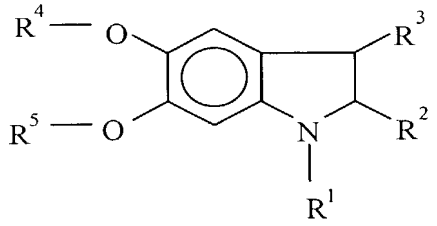
to be single compounds. On the contrary, other components may be present in small quantities in the hair colorants according to the invention due to the processes used to produce the individual dyes providing these other components do not adversely affect the coloring result or have to be ruled out for other reasons, for example toxicological reasons.

So far as the dyes suitable for use in the hair colorants and tinting compositions according to the invention are concerned, reference is also expressly made to the work by Ch. Zviak, **The Science of Hair Care, Chapter 7** (pages 248-250; substantive dyes) and **Chapter 8,** pages 264-267; oxidation dye precursors), published as Volume 7 of the Series **"Dermatology"** (Ed.: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986, and to the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel d.V., Mannheim.

Both the oxidation dye precursors and the substantive dyes are present in the preparations according to the invention in quantities of preferably 0.01 to 20% by weight and more preferably 0.5 to 5% by weight, based on the preparation as a whole.

Preferred precursors of natural dyes are indoles and indolines which contain at least one hydroxy or amino group, preferably as a substituent on the six-membered ring. These groups may carry further substituents, for example in the form of an etherification or esterification of the hydroxy group or an alkylation of the amino group.

Particularly suitable precursors of natural hair dyes are derivatives of 5,6-dihydroxyindoline corresponding to formula (Ia):



(Ia)

in which - independently of one another - R^1 is hydrogen, a C_{1-4} alkyl group or a C_{1-4} hydroxyalkyl group,

R^2 is hydrogen or a -COOH group, the -COOH group optionally being present as a salt with a physiologically compatible cation,

R^3 is hydrogen or a C_{1-4} alkyl group,

R^4 is hydrogen, a C_{1-4} alkyl group or a group -CO-R^6, where R^6 is a C_{1-4} alkyl group, and

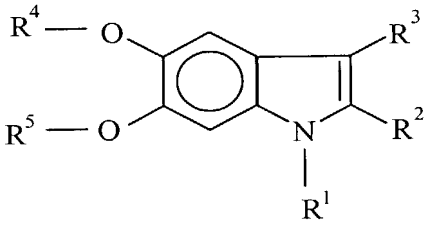
R^5 is one of the groups mentioned for R^4,

and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indoline are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid and 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and, in particular, 5,6-dihydroxyindoline.

Other particularly suitable precursors of natural hair dyes are derivatives of 5,6-dihydroxyindole corresponding to formula (Ib):



(Ib)

in which - independently of one another -

R^1 is hydrogen, a C_{1-4} alkyl group or a C_{1-4} hydroxyalkyl group,

R^2 is hydrogen or a -COOH group, the –COOH group optionally being

present as a salt with a physiologically compatible cation,

R^3 is hydrogen or a C_{1-4} alkyl group,

R^4 is hydrogen, a C_{1-4} alkyl group or a group -CO-R^6, where R^6 is a C_{1-4} alkyl group, and

R^5 is one of the groups mentioned for R^4,

and physiologically compatible salts of these compounds with an organic or inorganic acid.

Particularly preferred derivatives of indole are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

Within this group, particular emphasis is placed on N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole and, in particular, 5,6-dihydroxyindole.

The indoline and indole derivatives may be used both as free bases and in the form of their physiologically compatible salts with inorganic or organic acids, for example hydrochlorides, sulfates and hydrobromides, in the colorants used in the process according to the invention. The indole or indoline derivatives are present in these colorants in quantities of normally 0.05 to 10% by weight and preferably 0.2 to 5% by weight.

Where dye precursors of the indoline or indole type are used, it can be of advantage to use them together with at least one amino acid and/or at least one oligopeptide. Preferred amino acids are aminocarboxylic acids, more particularly α-aminocarboxylic acids and ω-aminocarboxylic acids. Among the α-aminocarboxylic acids, arginine, lysine, ornithine and histidine are particularly preferred. A most particularly preferred amino acid is arginine used more particularly in free form but also as the hydrochloride.

Hair colorants are normally adjusted to a mildly acidic to alkaline pH, i.e. to a pH of about 5 to 11, particularly where coloring is carried out oxidatively with atmospheric oxygen or other oxidizing agents, such as

hydrogen peroxide. To this end, the colorants contain alkalizing agents, normally alkali metal or alkaline earth metal hydroxides, ammonia or organic amines. Preferred alkalizing agents are monoethanolamine, monoisopropanolamine, 2-amino-2-methylpropanol, 2-amino-2-methyl-propane-1,3-diol, 2-amino-2-ethylpropane-1,3-diol, 2-amino-2-methyl-butanol and triethanolamine and alkali metal and alkaline earth metal hydroxides. Within this group, monoethanolamine, triethanolamine and 2-amino-2-methylpropanol and 2-amino-2-methylpropane-1,3-diol are preferred. ω-Amino acids, such as ω-aminocaproic acid, may also be used as alkalizing agents.

If the actual hair colors are developed in an oxidative process, typical oxidizing agents such as, in particular, hydrogen peroxide or adducts thereof with urea, melamine or sodium borate may be used. However, oxidation with atmospheric oxygen as sole oxidizing agent may be preferred. Oxidation may also be carried out with enzymes. In this case, the enzymes may be used both to produce oxidizing per compounds and to enhance the effect of an oxidizing agent present in small quantities. Thus, the enzymes (enzyme class 1: oxidoreductases) are capable of transferring electrons from suitable primary intermediates (reducing agents) to atmospheric oxygen. Preferred enzymes are oxidases, such as tyrosinase and laccase, although glucoseoxidase, uricase or pyruvate oxidase may also be used. Mention is also made of the procedure whereby the effect of small quantities (for example 1% and less, based on the composition as a whole) of hydrogen peroxide is strengthened by peroxidases.

The preparation of the oxidizing agent is preferably mixed with the preparation of the oxidation dye precursors immediately before coloring of the hair. The ready-to-use hair coloring preparation formed should have a pH value in the range from 6 to 10. In a particularly preferred embodiment, the hair colorant is used in a mildly alkaline medium. The application

temperatures may be in the range from 15 to 40°C but are preferably at the temperature of the scalp. After a contact time of about 5 to 45 and preferably 15 to 30 minutes, the hair colorant is removed from the hair to be colored by rinsing. There is no need for the hair to be washed with a shampoo where a carrier of high surfactant content, for example a coloring shampoo, has been used.

In the particular case of hair which is difficult to color, the preparation containing the oxidation dye precursors may be applied to the hair without preliminary mixing with the oxidation component. The oxidation component is applied after a contact time of 20 to 30 minutes, optionally after rinsing. After another contact time of 10 to 20 minutes, the hair is rinsed and, if desired, shampooed. In a first variant of this embodiment where the preliminary application of the dye precursors is intended to improve penetration into the hair, the corresponding formulation is adjusted to a pH value of about 4 to 7. In a second variant, oxidation with air is initially carried out, the formulation applied preferably having a pH value of 7 to 10. In the subsequent accelerated post-oxidation phase, it can be of advantage to use acidified peroxydisulfate solutions as the oxidizing agent.

Whichever of the processes mentioned above is used to apply the colorant according to the invention, development of the color may be supported and enhanced by adding certain metal ions to the colorant. Examples of such metal ions are Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+}, Li^{+}, Mg^{2+}, Ca^{2+} and Al^{3+}. Zn^{2+}, Cu^{2+} and Mn^{2+} are particularly suitable. Basically, the metal ions may be used in the form of a physiologically compatible salt. Preferred salts are the acetates, sulfates, halides, lactates and tartrates. Development of the hair color can be accelerated and the color tone can be influenced as required through the use of these metal salts.

The present invention also relates to the use of (A) at least one enzyme of the transglutaminase type and (B) at least one active substance

with substrate activity for the enzyme for improving the fastness to washing of colors on keratin fibers.

The present invention further relates to a two-part kit for coloring keratin fibers which contains a first preparation containing (a) a colorant composition and (b) an active substance with substrate activity and a second composition containing (c) an enzyme of the transglutaminase type.

The present invention also relates to a two-part kit for coloring keratin fibers which contains a first preparation containing (a) a colorant composition and (c) an enzyme of the transglutaminase type and a second composition containing (b) an active substance with substrate activity.

Finally, the present invention also relates to a three-part kit for coloring keratin fibers which contains (a) a colorant composition, (b) a composition containing an active substance with substrate activity and (c) a composition containing an enzyme of the transglutaminase type.

The following Examples are intended to illustrate the invention.

Examples

Example 1: color fixing of an oxidative color

a) Pretreatment

Kerling tresses (0.5 g Kerling, natural white) were subjected to five conventional permanent wave treatments with the commercial product "Poly Lock-Normale Dauerwelle". In the first step of a permanent wave treatment, the fibers were exposed to the reducing solution (containing 7.9% by weight thioglycolic acid) for 30 minutes at room temperature, rinsed with clean water and then fixed for 10 minutes at room temperature (oxidizing solution containing 2.6% by weight of hydrogen peroxide). After the oxidative treatment, the fibers were re-rinsed and dried.

b) Coloring

For coloring, a mixture of 1 g of a coloring crème (commercial product "Poly Diadem Pflége-Creme-Coloration Rotbuche" containing the dye precursors p-toluylene diamine, 2-aminomethyl-4-aminophenol, resorcinol and 5-amino-2-methylphenol) and 1 ml of an aqueous 6% hydrogen peroxide solution was applied to the tresses and left thereon for 30 mins. at 32°C. The hair was then rinsed, washed with a standard shampoo and dried.

c) Color fixing

To fix the color, the tresses were immersed at a temperature of 50°C first for 60 minutes in 2 ml of an aqueous casein solution (30 mg/ml, adjusted to pH 7.6 with tris(hydroxymethyl)aminomethane (TRIS) HCl buffer) and then for 60 minutes in 2 ml of an aqueous transglutaminase solution (50 mg/ml Activa® WM[1], corresponding to 0.5 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer).

[1] powder form commercial product, 1% by weight transglutaminase in 9% by weight dextrin

d) Testing of fastness to washing

Finally, to test fastness to washing, the tresses were washed with a standard shampoo and dried. The washing process was carried out in all six times.

The color of the tresses was measured colorimetrically at 4 points with a Datacolor Text Flash (manufacturer: Data Color International). The results were evaluated with the Data Color Tools Software QC in accordance with formula (I) below and are set out in the following Table. The color of a tress after treatment steps a), b) and d) was used as reference (test 1a, no color fixing).

$$\frac{K/S_{Sample}}{K/S_{Reference}} * 100 = Coloringstrength[\%] \qquad (I)$$

where

K = absorption coefficient

S = scattering coefficient

K/S = reflection coefficient.

In addition, the ΔE value of the CIELAB color system was determined in accordance with formula (II):

$$\Delta E = \Delta E = \sqrt{(\Delta L)^2 + (\Delta A)^2 + (\Delta B)^2} \qquad (II)$$

	Tress treatment	ΔE	Coloring strength in %
Test 1a	Steps a), b) and d)	0	100
Test 1b	Steps a), b), c) and d)	6.14	138

The tresses treated with transglutaminase and casein felt "set", even after shampooing. The tresses treated with casein only, i.e. not with transglutaminase, did not show this effect after shampooing.

Example 2: color fixing of an oxidative color

a) Pretreatment

Kerling tresses (0.5 g Kerling, natural white) were subjected to two conventional permanent wave treatments with the commercial product "Poly Lock-Normale Dauerwelle". In the first step of a permanent wave treatment, the fibers were exposed to the reducing solution (containing 7.9% by weight thioglycolic acid) for 30 minutes at room temperature,

rinsed with clean water and then fixed for 10 minutes at room temperature (oxidizing solution containing 2.6% by weight of hydrogen peroxide). After the oxidative treatment, the fibers were re-rinsed and dried.

b) Coloring

For coloring, a mixture of 1 g of a coloring crème (commercial product "Poly Diadem Pflege-Creme-Coloration Rotbuche" containing the dye precursors p-toluylene diamine, 2-aminomethyl-4-aminophenol, resorcinol and 5-amino-2-methylphenol) and 1 ml of an aqueous 6% hydrogen peroxide solution was applied to the tresses and left thereon for 30 mins. at 32°C. The hair was then rinsed, washed with a standard shampoo and dried.

c) Color fixing

To fix the color, the tresses were immersed at a temperature of 50°C first for 60 minutes in 2 ml of an aqueous soya solution (30 mg/ml, adjusted to pH 7.6 with TRIS HCl buffer) and then for 60 minutes in 2 ml of an aqueous transglutaminase solution (50 mg/ml Activa® WM, corresponding to 0.5 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer).

In test 2c), the tresses were immersed for 60 minutes at a temperature of 35°C in 2 ml of an aqueous soya solution (30 mg/ml, adjusted to pH 7.6 with TRIS HCl buffer) to which 100 µl of an aqueous transglutaminase solution (50 mg/ml Activa® WM, corresponding to 0.5 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer) had been added.

d) Testing of fastness to washing

Finally, to test fastness to washing, the tresses were washed with a standard shampoo and dried. The washing process was carried out in all six times.

As described above, the color of the tresses was measured colorimetrically at 4 points. The results are set out in the following Table. The color of a tress after treatment steps a), b) and d) was used as reference (test 2a, no color fixing).

	Tress treatment	Coloring strength in %
Test 2a	Steps a), b) and d)	100
Test 2b	Steps a), b), c) and d)	110
Test 2c	Steps a), b), c) and d)	105

The tresses treated with transglutaminase and casein felt slightly more "set", even after shampooing. The tresses treated with soya only, i.e. not with transglutaminase, did not show this effect after shampooing.

Example 3: color fixing of a temporary color

a) Pretreatment

Kerling tresses (0.5 g Kerling, natural white) were subjected to two blonding treatments with the commercial product "Poly Blonde Intensivaufheller Ultra" (oxidation by 5.3% by weight hydrogen peroxide and 10.7% by weight ammonium peroxodisulfate) and to two permanent wave treatments with the commercial product "Poly Lock-Normale Dauerwelle". In the first step of a permanent wave treatment, the fibers were exposed to the reducing solution (containing 7.9% by weight thioglycolic acid) for 30 minutes at room temperature, rinsed with clean water and then fixed for 10 minutes at room temperature (oxidizing solution containing 2.6% by weight of hydrogen peroxide). After the oxidative treatment, the fibers were re-rinsed and dried.

b) Coloring

1 g of the coloring cream "Live Soft Toner Kastanie" (containing the

dyes 6-chloro-4-nitro-2-aminophenol, HC Blue No. 2 and HC Red N. 3) was then applied to the tresses and left thereon for 30 minutes at 32°C. The hair was then rinsed, washed with a standard shampoo and dried.

c) Color fixing

To fix the color, the tresses were immersed at a temperature of 50°C first for 60 minutes in 2 ml of an aqueous casein solution (30 mg/ml, adjusted to pH 7.6 with TRIS HCl buffer) and then for 60 minutes in 2 ml of an aqueous transglutaminase solution (50 mg/ml Activa® WM, corresponding to 0.5 mg/ml active substance, adjusted to pH 7.6 with TRIS HCl buffer).

d) Testing of fastness to washing

Finally, to test fastness to washing, the tresses were washed with a standard shampoo and dried. The washing process was carried out in all three times.

As described above, the color of the tresses was measured colorimetrically at 4 points. The results are set out in the following Table. The color of a tress after treatment steps a), b) and d) was used as reference (test 3a, no color fixing).

	Tress treatment	ΔE	Coloring strength in %
Test 3a	Steps a), b) and d)	0	100
Test 3b	Steps a), b), c) and d)	1.52	110

The tresses treated with transglutaminase and casein felt "set", even after shampooing. The tresses treated with casein only, i.e. not with transglutaminase, did not show this effect after shampooing.

CLAIMS

1. A process for coloring keratin fibers with dyes and/or dye precursors, characterized in that

(A) at least one enzyme of the transglutaminase type and

(B) at least one active substance with substrate activity for the enzyme

are applied to the fibers.

2. A process as claimed in claim 1, characterized in that the enzyme is a calcium-independent transglutaminase.

3. A process as claimed in claim 1 or 2, characterized in that the active substance with substrate activity is a protein or a protein hydrolyzate.

4. A process as claimed in claim 3, characterized in that the active substance with substrate activity is selected from casein, soya protein and wheat protein.

5. A process as claimed in claim 1 or 2, characterized in that the active substance with substrate activity is an active substance synthetically functionalized with an H_2N-R group or an H_2N-(CO)-R' group, where R and R' stand for an unbranched C_{1-8} alkylene group.

6. A process as claimed in claim 5, characterized in that the active substance with substrate activity carries at least one H_2N-$(CH_2)_4$ group.

7. A process as claimed in claim 5, characterized in that the active substance with substrate activity carries at least one H_2N-(CO)-CH_2-CH_2 group.

8. A process as claimed in any of claims 1 to 7, characterized in that, in a first step, the coloring preparation and, in a second step, the enzyme preparation together with the active substance with substrate activity are applied to the fibers.

9. A process as claimed in any of claims 1 to 8, characterized in that the contact time is 3 to 120 minutes.

10. A process as claimed in any of claims 1 to 9, characterized in that the fibers are pretreated before the coloring process.

11. A process as claimed in claim 10, characterized in that the fibers are pretreated with an oxidizing agent.

12. A process as claimed in claim 10, characterized in that the fibers are pretreated with a reducing agent.

13. A process as claimed in claim 10, characterized in that the fibers are pretreated with an enzyme.

14. The use of (A) at least one enzyme of the transglutaminase type and (B) at least one active substance with substrate activity for the enzyme for improving the fastness to washing of colors on keratin fibers.

15. A two-part kit for coloring keratin fibers, characterized in that it contains a first preparation containing (a) a colorant composition and (b) an active substance with substrate activity and a second composition containing (c) an enzyme of the transglutaminase type.

16. A two-part kit for coloring keratin fibers, characterized in that it contains a first preparation containing (a) a colorant composition and (c) an enzyme of the transglutaminase type and a second composition containing (b) an active substance with substrate activity.

17. A three-part kit for coloring keratin fibers, characterized in that it contains (a) a colorant composition, (b) a composition containing an active substance with substrate activity and (c) a composition containing an enzyme of the transglutaminase type.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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siehe PCT Gazette Nr. 27/2001 vom 5. Juli 2001, Section II

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR COLORING KERATIN FIBERS BY MEANS OF AT LEAST ONE ENZYME OF THE TRANSGLUTAMINASE TYPE

(54) Bezeichnung: VERFAHREN ZUR FÄRBUNG KERATINISCHER FASERN MINDESTENS EIN ENZYM VOM TYP DER TRANSGLUTAMINASE

(57) Abstract: The invention relates to a method for coloring keratin fibers with dyes and/or pre-dyes. According to the inventive method, (A) at least one enzyme of the transglutaminase type and (B) at least one active substance that has a substrate activity for the enzyme are applied on the fibers. The inventive method substantially improves the color fastness properties, especially the fastness to washing of the colorations obtained with said dyes.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Färbung keratinischer Fasern mit Farbstoffen und/oder Farbstoffvorprodukten, bei dem auf die Fasern (A) mindestens ein Enzym vom Typ der Transglutaminase und (B) mindestens ein Wirkstoff, der eine Substrataktivität für das Enzym aufweist, aufgebracht werden. Mithilfe dieses Verfahrens können die Echtheitseigenschaften, insbesondere die Waschechtheit, der erzielten Färbungen deutlich verbessert werden.

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PTO/SB/01 (6-95)
Approved for use through: 10/31/98 OMB 0651-0032
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Rev. 6/95

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Patent and Trademark Office

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number	H 3609 PCT/US
First Named Inventor	Kleen, Astrid
COMPLETE IF KNOWN	
Application Number	10/088,247
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:
My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR COLORING KERATIN FIBERS

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 09/13/2000 as United States Application Number or PCT International Application Number PCT/EP00/08923 and was amended on (MM/DD/YYYY) (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1 56

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
199 45 486.8	DE	09/22/1999	☐	☐	☒

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.
		☐

Burden Hour Statement This form is estimated to take 4 hours to complete. Time will vary depending upon the needs of the individual case Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231 DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS SEND TO: Assistant Commissioner for Patents, Washington DC 20231

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DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United Sates of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112 1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*
	PCT/EP00/08923	09/13/2000	

☐ Additional U S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name OR ____ Customer Number ____ or label ____

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name	**Astrid**	Middle Initial		Family Name	**Kleen**	Suffix e.g. Jr.	
Inventor's Signature	/Astrid Kleen/				Date	22.03.02	
Residence: City	**Erkrath**	State		Country	**Germany**	Citizenship	**Germany**
Post Office Address	**Nordstrasse 17**						
Post Office Address							
City	**40699 Erkrath**	State		Zip		Country	**Germany**	Applicant Authority	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

Type a plus sign (+) inside this box → ☐ H 3609 PCT/US

DECLARATION

ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Andrea	Middle Initial		Family Name	Saettler	Suffix e.g. Jr.	
Inventor's Signature	Andrea Saettler				Date	3.4.2002	
Residence: City	Duesseldorf	State		Country	Germany	Citizenship	Germany
Post Office Address	Himmelgeisterstr. 187						
Post Office Address							
City	40225 Duesseldorf	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Horst	Middle Initial		Family Name	Hoeffkes	Suffix e.g. Jr.	
Inventor's Signature	Horst Hoeffkes				Date	20.3.02	
Residence: City	Duesseldorf	State		Country	Germany	Citizenship	Germany
Post Office Address	Carlo-Schmid-Str. 113						
Post Office Address							
City	40595 Duesseldorf	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Ralf	Middle Initial		Family Name	Otto	Suffix e.g. Jr.	
Inventor's Signature					Date	29.04.02	
Residence: City	~~Bad Friedrichshall~~	State		Country	Germany	Citizenship	Germany
Post Office Address	Oedheimer Str. 6						
Post Office Address							
City	74177 Bad Friedrichshall	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country		Applicant Authority	

☐ Additional inventors are being named on supplemental sheet(s) attached hereto